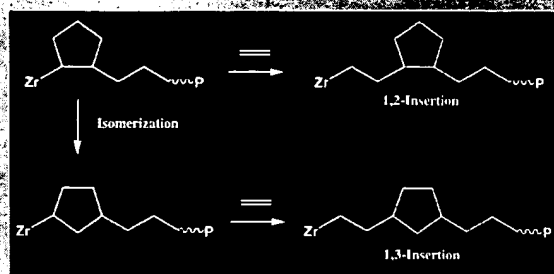


Full Paper: Copolymerization of ethylene and cyclopentene (CPE) was carried out with various non-bridged and bridged zirconocene catalysts using methylaluminoxane as a cocatalyst. Non-bridged metallocene catalysts effected ethylene homopolymerization without copolymerization. On the other hand, bridged zirconocene catalysts produced copolymers containing *cis*-1,2-cyclopentane units. Among the used catalysts, *rac*-ethylenebis(indenyl)zirconium dichloride [Et(Ind)₂ZrCl₂] gave copolymers containing the highest amount of CPE units by 1,2-insertion or 1,3-insertion. Temperature-rising elution fractionation of the copolymers using 1,2-dichlorobenzene as a solvent showed a broad distribution of copolymer com-

position in copolymers obtained by specific zirconocene catalysts.



Copolymerization of Ethylene and Cyclopentene with Zirconocene Catalysts: Effect of Ligand Structure of Zirconocenes

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Keywords: copolymerization; cyclopentene; effect of ligand; ethylene; zirconocene catalyst

Introduction

Metallocene catalysts are effective not only for the polymerization of common olefins, such as ethylene and propylene, but for the polymerization of cycloolefins.^[1] Cycloolefins, such as cyclobutene and norbornene, can be polymerized via 1,2-propagation by some metallocene catalysts. On the other hand, cyclopentene is polymerized via a 1,3-insertion mechanism. The resulting polycycloolefins show extremely high melting points over 400 °C.

Copolymerization of cycloolefin with ethylene or propylene is an effective method to control thermal properties of polycycloolefins.^[2] Olefin copolymers containing cyclic structures have been developed for optical materials with high glass-transition temperature. Especially, poly(ethylene-*co*-norbornene) is a well-known and useful amorphous copolymer with high transparency. Kaminsky and Spiehl investigated the copolymerization of ethylene with monocyclic olefins, such as cyclopentene (CPE), cycloheptene and cyclooctene, with a zirconocene catalyst, *rac*-ethylenebis(indenyl)zirconium dichloride, combined with a cocatalyst methylaluminoxane (MAO).^[3] They reported that cycloolefins were incorporated via 1,2-insertion mechan-

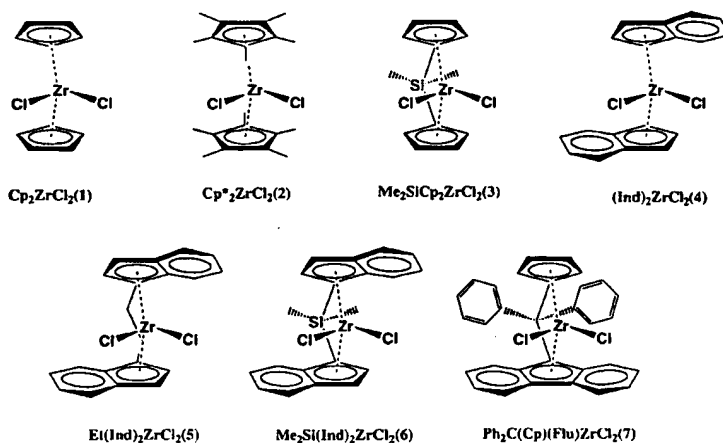
ism without a ring-opening reaction. Müller and coworkers investigated copolymerization of ethylene and CPE with a specific zirconocene catalyst, *rac*-dimethylsilylene(ferrocene[2,3]indenyl)(cyclopentadienyl)zirconium dichloride, and detected 1,3-type CPE units in the resulting copolymer by detailed NMR studies.^[4] The propagation mode of CPE in the copolymerization with ethylene undoubtedly affects the property of poly(ethylene-*co*-CPE). Control of CPE behaviors, that is, propagation mode and relative reactivity, in the copolymerization with ethylene should be essential for precise synthesis of poly(ethylene-*co*-CPE).

In this study, we carried out the copolymerization of ethylene and CPE with various zirconocene catalysts, investigating the effect of the ligand structure of zirconocene catalysts on the monomer reactivity and the mechanism of CPE polymerization.

Experimental Part

Materials

Zirconocene catalysts were commercially obtained from Aldrich Co., Ltd. and Boulder Science Co., Ltd., and used without further purification. A list of zirconocene catalysts is



Scheme 1.

shown in Scheme 1. A hexane solution of methylisobutylaluminumoxane (MMAO) was donated from Tosoh Akzo Co., Ltd. and used without further purification. CPE (Tokyo Kasei) was dried with CaH_2 . Ethylene (Sumitomo Seika) was purified by passing it through columns of NaOH , P_2O_5 and molecular sieves 3 Å.

Copolymerization

The copolymerization of ethylene and CPE was carried out in a 100 mL glass reactor equipped with a magnetic stirrer. Toluene was added to the reactor under nitrogen atmosphere. Ethylene was introduced into the reactor at 40°C under 1 atm until the solvent was saturated with ethylene, and a measured amount of CPE was added. MMAO and a zirconocene catalyst were premixed in a 50 mL glass flask at 25°C within 5 min. Polymerization was started by introducing the catalyst solution into the reactor. The polymerization was terminated by adding a small amount of ethanol. The polymer obtained was extracted with boiling 1,2-dichlorobenzene to remove catalyst residues. The solution of extracted polymer was concentrated by evaporation and precipitated in a large excess of ethanol. The precipitate was recovered by filtration and dried in vacuo at 60°C for 6 h.

Analytical Procedures

Molecular weight and molecular weight distribution of the copolymer were measured at 140°C by means of gel permeation chromatography (Tosoh HLC-8121 GPC/HT) using 1,2-dichlorobenzene as a solvent and calibrated with standard polystyrene samples. ^1H and ^{13}C NMR spectra were recorded at 130°C on a JEOL Lambda-400 Fourier transform NMR spectrometer in 5 wt.-% trichlorobenzene/benzene- d_6 (9/1, v/v). Melting temperatures were measured by a Seiko DSC6200 (Seiko Instruments Inc.) at a heating rate of 10 K/min after preheating to 200°C following precooling to -150°C. Temperature-rising elution fractionation (TREF) was carried out with cross fractionation chromatography (Dia-instruments CFCT-150C) using 1,2-dichlorobenzene as a solvent.

Results and Discussion

Copolymerization of ethylene and CPE was carried out with various zirconocene catalysts using MMAO as a cocatalyst at 40°C. Results of the copolymerization are summarized in Table 1. When the copolymerization was carried out with non-bridged zirconocene catalysts, 1, 2 and 4, polyethylene without incorporation of CPE was obtained. On the other hand, bridged zirconocene catalysts produced copolymers in good yields. The CPE content in the copolymer, which was determined by ^1H NMR spectroscopy, increased with increasing CPE in the feed. The structure of inserted CPE units in the copolymers was investigated by ^{13}C NMR spectroscopy. Figure 1 (a) and (b) show the ^{13}C NMR spectra of the copolymers with low CPE content obtained with isospecific catalysts 5 and 6, respectively. Scheme 2 illustrates the structures of the copolymer corresponding to the ^{13}C NMR spectra in Figure 1 (a) and (b). The signals at 43.3 (1, 2), 31.2 (3, 5), and 23.2 (4) ppm are assigned to isolated *cis*-1,2-cyclopentane units in the ethylene sequence.^[3,4,5] Other signals are observed in the spectrum of a copolymer prepared by 5 (Figure 1 (a)). Those at 41.1 (2'), 40.6 (1',3'), and 32.2 (4',5') ppm are assignable to the isolated *cis*-1,3-cyclopentane units.^[5] The 1,3-substituted cyclopentane structure can be explained by isomerization of 1,2-substituted cyclopentane terminal preceding ethylene insertion, as shown in Scheme 3. This mechanism is similar to the 1,3-type polymerization of propylene with some metallocene catalysts.^[6] Copolymer obtained with aspecific catalyst 3 and syndiospecific catalyst 7 contained only *cis*-1,2-cyclopentane structure. These results indicate that the preferential mode of CPE polymerization is 1,2-type and that stereospecificity of the zirconocene catalysts does not affect the polymerization mode of CPE in the copolymerization.

Figure 2 shows the copolymer composition curves of ethylene/CPE copolymers obtained with bridged zircono-

Table 1. Results of ethylene/cyclopentene(CPE) copolymerization with zirconocene catalysts. Polymerization conditions: MMAO[Al]/[Zr], 1000; ethylene, 1.0 atm; polymerization temperature, 40 °C.

Run	Catalyst		CPE mol/L	Time min	Polymer yield kg/mol Zr · h	CPE in copolymer ^{a)} mol-%	1,3-Insertion CPE units ^{b)} %	$\bar{M}_n \times 10^{-4}$ ^{c)}	\bar{M}_w/\bar{M}_n ^{d)}	T_m ^{d)} °C
	Nature	mmol/L								
1	1	0.04	1.14	20	1340	0.0	—			
2	2	0.1	0.57	10	1560	0.0	—			
3	3	0.1	0.57	10	1090	2.1	0.0	2.7	3.3	
4		0.1	1.14	30	440	3.1	0.0	2.1	3.6	123.9, 103.1
5		0.2	2.27	45	220	6.5	0.0	1.1	2.7	
6		0.2	5.68	120	16.4	24.6	17.3			
7	4	0.1	0.57	6	1220	0.0	—			
8	5	0.1	0.23	6	1670	4.4	23.5	4.0	3.5	
9		0.1	0.45	6	2270	6.2	24.1	3.9	3.2	119.2, 75.7
10		0.1	0.57	5	4430	15.1	26.2	2.5	2.6	
11		0.1	1.14	5	4810	22.3	31.2	2.1	3.0	
12		0.1	2.27	6	4980	32.2	23.9	1.0	5.1	
13		0.1	5.68	15	1540	37.8	9.5	0.44	3.2	
14	6	0.04	0.57	20	2340	3.5	0.0	13.3	2.6	102.8
15		0.04	1.14	30	1230	4.8	0.0	7.2	2.3	
16		0.04	2.27	10	6720	12.9	0.0	5.8	1.9	
17		0.1	5.68	12	1840	27.5	5.6			
18	7	0.1	0.57	15	900	2.5	0.0	4.8	2.0	106.9
19		0.1	1.14	15	920	6.1	0.0	7.3	1.9	
20		0.1	2.27	60	340	13.4	0.0	6.5	1.8	
21		0.2	5.68	180	28.1	22.4	6.2	1.4	2.2	

^{a)} Determined by ¹H NMR spectroscopy.

^{b)} Determined by ¹³C NMR spectroscopy.

^{c)} Determined by GPC using polystyrene standard.

^{d)} Measured by DSC.

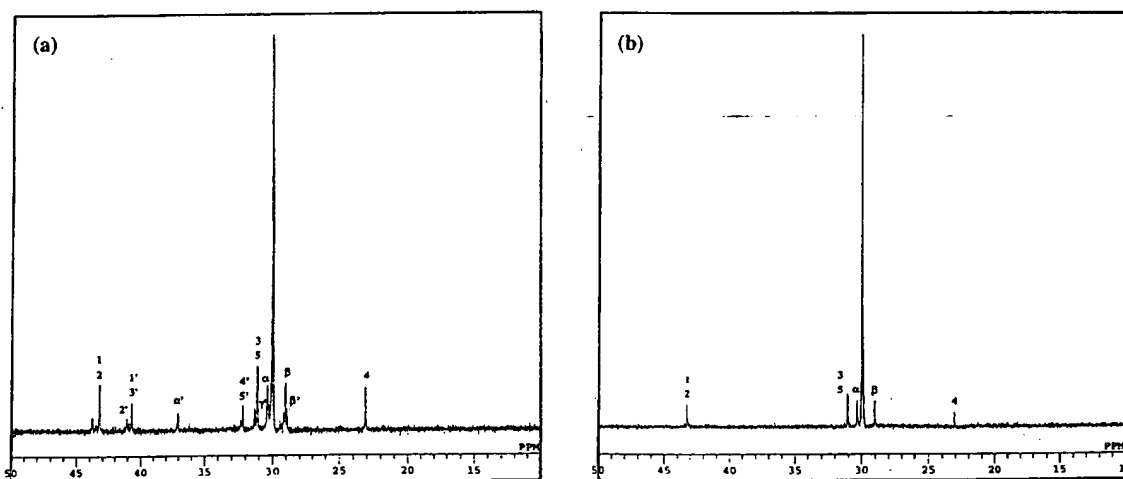
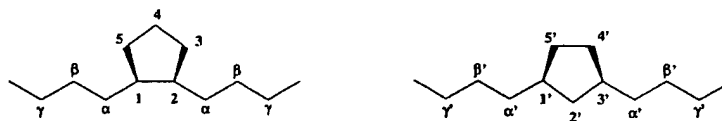


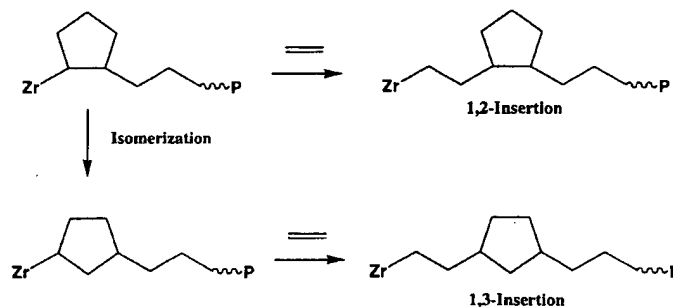
Figure 1. ¹³C NMR spectra of poly(ethylene-co-CPE) obtained with bridged zirconocene catalysts: (a) 5 (Run 10), (b) 6 (Run 15).

cene catalysts. Ethylene is more reactive than CPE and the highest incorporation of CPE was attained in the copolymerization with the catalyst 5. Monomer reactivity ratios were determined by the Fineman–Ross plot, r_E being 239 (3), 21.9 (5), 143 (6), and 235 (7).

The copolymerization of ethylene and CPE was carried out at high CPE feed to obtain CPE-rich copolymers (Runs 6, 12, 13, 17, and 21). Monomer sequence distributions of the resulting copolymers with high CPE content (more than 20 mol-%) were investigated by ¹³C NMR



Scheme 2.



Scheme 3.

Table 2. Monomer sequence distribution of poly(ethylene-co-CPE) obtained with bridged zirconocene catalysts. E = ethylene, C = CPE.

Run	Catalyst	CPE mol-%	EEE	EEC + CEE	ECE	CEC	ECC + CCE	CCC	EE	EC	CC
6	3	24.6	0.394	0.341	0.134	0.019	0.112	0.0	0.564	0.379	0.056
12	5	32.2	0.133	0.446	0.322	0.099	0.0	0.0	0.356	0.644	0.0
13	5	37.8	0.088	0.551	0.308	0.040	0.014	0.0	0.363	0.630	0.007
17	6	27.5	0.243	0.446	0.239	0.030	0.043	0.0	0.446	0.506	0.048
21	7	22.4	0.320	0.464	0.224	0.0	0.0	0.0	0.552	0.448	0.0

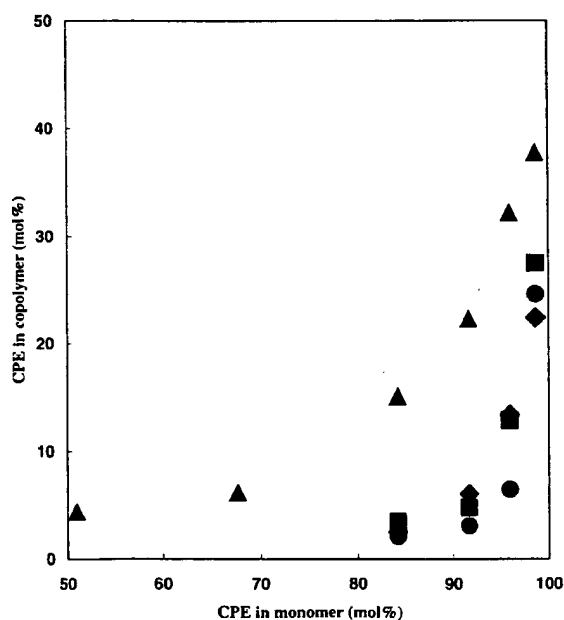


Figure 2. Copolymerization diagrams of ethylene and CPE with bridged zirconocene catalysts: 3 (●), 5 (▲), 6 (■), 7 (◆).

spectroscopy, and the results are presented in Table 2. [CCC] sequence, where C represents CPE unit, was not detected in any copolymers, and [CC] dyad was not found in copolymers obtained with the catalysts 5 and 7. These results indicate that it is difficult to react the CPE monomer with a CPE growing end. This tendency becomes clearer in copolymerizations with the catalysts 5 and 7.

Figure 3 shows the relationship between CPE content and the molar content of 1,3-disubstituted cyclopentane unit in the copolymer. The 1,3-disubstituted cyclopentane units are detected in the copolymers containing more than 20 mol-% of CPE which were obtained with the catalysts 3, 6 and 7. When the copolymerization was carried out under low CPE feed using the same catalysts, 1,3-insertion did not occur. These results indicate that isomerization of 1,2-substituted cyclopentane terminal to 1,3-substituted one proceeds only at high CPE feed, in other words, low ethylene feed, as illustrated in Scheme 2. The content of 1,3-substituted cyclopentane units should increase with decreasing ethylene feed or with increasing CPE feed.

The catalyst 5 showed peculiar behaviors in the copolymerization of ethylene and CPE that the content of 1,3-disubstituted cyclopentane units was fairly high in the

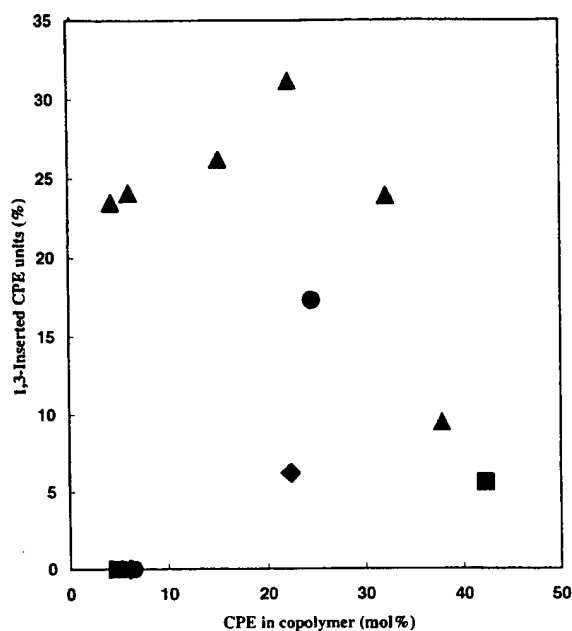
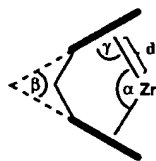
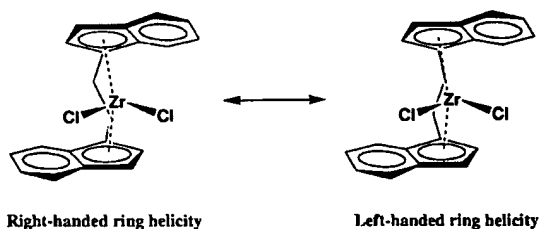
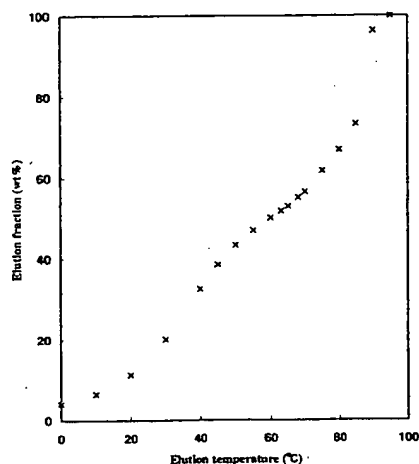


Figure 3. Relationship between CPE content and molar content of 1,3-disubstituted cyclopentane unit in the copolymer obtained with bridged zirconocene catalysts 3 (●), 5 (▲), 6 (■), and 7 (◆).



Scheme 4.

copolymers obtained under low CPE feed conditions and, after reaching the maximum content, decreased sharply with increasing CPE content in the copolymer. The sym-



Scheme 5.

metry of bridged zirconocene catalysts may play an important role in determining the reactivity and mechanism of CPE insertion. To test this possibility, crystallographic parameters were compared: 5; $\alpha = 125.3^\circ$, $\beta = 60.4^\circ$, $\gamma = 87.2^\circ$, $d(\text{Zr-Cp}) = 2.44\text{--}2.62 \text{ \AA}$;[7] 6; $\alpha = 127.8^\circ$, $\beta = 60.2^\circ$, $\gamma = 85.7^\circ$, $d = 2.46\text{--}2.66 \text{ \AA}$,[8] where α , β , γ and d are angle of $\text{cp-Zr-cp}'$ (cp, cp' = centroids of the Cp rings, Cp = cyclopentadienyl moiety in the indenyl ligand), angle between Cp planes, angle between Cp plane and cp-Zr bond, and length of cp-Zr , respectively, as shown in Scheme 4. The catalyst 5 shows a somewhat smaller α angle and a larger γ angle than those of the catalyst 6. This difference means that the coordination space of the catalyst 5 is wider than that of the catalyst 6. Another possibility is a distortion of indenyl ligands of the catalyst 5 due to internal rotation of the ethylidene bridge. The catalyst 5 forms either right-handed or left-handed ring helix (Scheme 5) as reported by Kaminsky et al.[9] The internal rotation between right-hand and left-hand structure widens β and γ angles and narrows α angle. The rotation leaves wider coordination space in the catalyst 5. However, the facile 1,3-insertion of CPE by the catalyst 5 can not be explained in this way.

Thermal properties of the copolymers with low CPE content were investigated. Multiple melting endotherms were observed in the copolymers obtained with the cata-

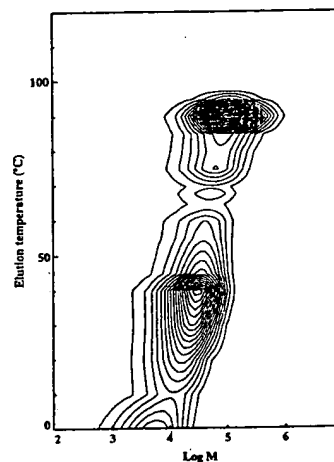


Figure 4. TREF and CFC diagrams of poly(ethylene-co-CPE) obtained with the catalyst 5 (Run 9).

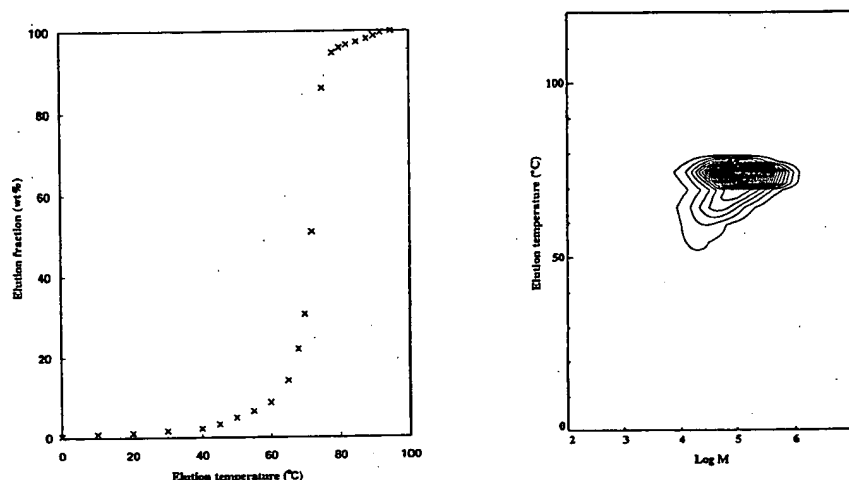


Figure 5. TREF and CFC diagrams of poly(ethylene-*co*-CPE) obtained with the catalyst 6 (Run 14).

lysts 3 and 5. TREF of the copolymers was measured with CFC-IR to elucidate the composition distribution of the copolymers. Figure 4 and 5 show the TREF diagrams together with contour-type CFC diagrams of the copolymers obtained with the catalysts 5 and 6, respectively. Figure 4 indicates that the copolymer obtained with the catalyst 5 is composed of three types of polymers; the first is extracted below 10°C, the second from 10°C to 70°C, and the third above 70°C. The structures of ODCB-elution fractions below and above 70°C were investigated by NMR spectroscopy. The CPE contents of the low temperature (below 70°C) and high temperature (above 70°C) elution fractions were 9.9 mol-% and 2.9 mol-%, respectively. The contents of 1,3-disubstituted CPE units of both fractions were almost the same. The difference of elution temperature is derived from the difference of the CPE content. On the other hand, the copolymer obtained with the catalyst 6 was extracted around 80°C as shown in Figure 5, and a narrow distribution of the copolymer composition was confirmed.

Metallocene catalysts have been shown to produce uniform active species and to produce polyolefins with narrow distribution of molecular weight and composition. However, Soga et al. found a heterogeneous composition of poly(ethylene-*co*-1-hexene) obtained with typical metallocene catalysts.^[10] The active species of metallocene-MAO systems have been analyzed by various methods, and some kinds of active species have been detected. Cam et al. observed reduction of Zr(IV) to Zr(III) in 1-MAO system.^[11] Tritto et al. detected two kinds of ion pairs, i.e., monomeric and dimeric ones, in the Cp_2TiCH_3Cl -MAO system.^[12] It is considered that a heterogeneous composition of the copolymer prepared by a metallocene catalyst should be derived from heterogeneity of the active sites in the copolymerization. The same

explanation could be applied to the poly(ethylene-*co*-CPE) obtained with the catalysts 3 and 5. A further study is, however, necessary to clarify the relationship between molecular structure of zirconocene and distribution of copolymer composition.

Conclusion

Poly(ethylene-*co*-CPE) was successfully obtained with bridged zirconocene catalysts. The CPE was preferentially incorporated via 1,2-insertion. The catalyst 5 gave the copolymer with the highest content of CPE incorporated by 1,3-insertion. TREF of the copolymers showed the distribution of copolymer composition obtained with the catalysts 3 and 5.

Received: June 4, 2001

Revised: August 16, 2001

Accepted: August 20, 2001

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